

THE DISTRIBUTION OF OXYGEN-CONTAINING FUNCTIONAL GROUPS IN PITCH  
FROM A HIGH-TEMPERATURE COAL TAR

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INTRODUCTION

The phenolic hydroxyl content of coal tar pitch is mainly confined to the portion insoluble in light petroleum. In this portion there is approximately one phenolic group per molecule of pitch constituent - indicating that the phenolic hydroxyl, although small in percentage, is a significant (1) constituent. It has been shown (2) that, for a series of pitch fractions prepared from coke-oven, vertical-retort, and low-temperature tars, 40 to 68 per cent of the oxygen in the benzene-soluble, light-petroleum-insoluble fractions and 28 to 63 per cent of the oxygen in the pyridine-soluble, benzene-insoluble fractions is in the form of phenolic groups.

The present paper describes a systematic study of the oxygen-containing groups in a pitch from a high-temperature tar obtained by carbonizing a medium-volatile bituminous coal at 1000°C. in a technical-scale plant simulating conditions in a by-product coke-oven. An attempt has been made to account for all the oxygen, other than ethereal oxygen, in the pitch and to relate the concentration of the various functional groups to the molecular size of the pitch fraction.

EXPERIMENTAL

A. Preparation of Pitch and Pitch Fractions

A pitch of softening point 66°C. (K. and S.) was prepared by rapid distillation (70 grams per minute) of a 5-kilogram charge of tar in a metal still of the S.T.P.T.C.\* type - a method believed to yield a pitch similar to those produced industrially in pipe stills (3).

The pitch was separated into four fractions by solvent extractions:

- (i) "Crystalloids" - soluble in light petroleum (b.p. 60 to 80°C.).
- (ii) "Resinoids" - insoluble in light petroleum but soluble in benzene.
- (iii) "C<sub>2</sub>" - insoluble in benzene but soluble in pyridine.
- (iv) "C<sub>1</sub>" - insoluble in pyridine.

The C<sub>2</sub> fractions were further separated by fractional precipitation of a pyridine solution of the C<sub>2</sub> with water.

All separations and functional-group analyses were carried out in darkness and in an atmosphere of nitrogen.

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\* Standardization of Tar Products Tests Committee (Great Britain).

## B. Determination of Functional Groups

### 1. Phenolic Groups

I. Non-aqueous titration. - Mixtures of the sample (0.1 to 0.5 gram) with 2,6-xylenol (0.01 to 0.02 gram) were titrated potentiometrically in pyridine solution (or suspension) with 0.2N sodium aminoethoxide in ethylene diamine as described by Greenhow and Smith (4). By co-titration with xylenol it is possible to estimate phenolic groups not normally giving a sharp end point in the absence of this reagent, but in addition the method gives an estimate of the carboxyl, phenolic ester, phenolic lactone, and some quinone groups. Carbon dioxide and carboxylic acids give a separate inflexion in the titration curve (4), and may be allowed for; the inflexion is sharpened by the addition of benzoic acid to the sample (see 3, II below). Titrations were reproducible within 10 per cent.

II. Mesylation. - The sample (0.8 to 1 gram) in pyridine (50 ml.) was treated at 0 to 5°C. with freshly distilled methane sulphonyl chloride (7 ml.) for about 24 hours, the mixture poured into ice water (200 ml.) and acidified with 5N hydrochloric acid, the precipitate washed with 5N hydrochloric acid and, finally, with water, and dried in vacuo at 50°C. The hydroxyl content was measured from the increase in sulphur content of the sample; reproducibility was about four per cent. It was found that various pure compounds, including heterocyclic tertiary amines, quinones, esters, lactones, and carbazole derivatives, did not react with methane sulphonyl chloride under the conditions used. A low mesylation value was obtained with indole, probably by the addition of part of the reagent molecule to chains of indole polymer. Primary amines, secondary aliphatic amines, and alcohols react to give the expected mesyl derivatives.

III. Methylation. - Diazomethane in ether was used as the reagent, a 1:1 mixture of dry ether and benzene as the solvent for the pitch fraction, and methanol as the catalyst. The methylated product was separated into two fractions, one being insoluble and the other soluble in the reaction medium. Methoxyl determinations were carried out on the methylated sample before and after hydrolysis (with N hydrochloric acid) for measurement of the carboxylic acid content.

IV. Acetylation. - The technique used was that of Blom et al. (5) in which the sample is first treated with acetic anhydride in pyridine, the acetylated product is then hydrolysed with barium hydroxide, and finally the acetic acid is distilled from the acidified solution and titrated. The acetic acid distilled irregularly from hydrolysed acetylated crystalloids and resinoids, indicating that further hydrolysis, possibly of N-acetyl compounds, was taking place in the acid solution.

V. Methylation followed by acetylation. - Processes III and IV were used, in series.

VI. Acetylation followed by methylation. - Processes IV and III, in that order.

### 2. Carbonyl Groups

The method used was that of Blom et al. (5), in which hydroxylamine hydrochloride is the reagent. Oxime formation was measured in three ways, namely from (i) the increase in nitrogen content, (ii) the decrease in nitrogen content on hydrolysis of oxime, and (iii) determination of hydrolysable oxime as ammonia. Application of the method to pitch samples gave a reproducibility of about eight per cent.

### 3. Carboxylic Acids

These were determined by the hydrolysis of methylated samples (1, III above) and by two additional methods:

I. Decarboxylation. - A semi-micro procedure similar to that of Beroza (6) was used but with a larger sample (0.4 gram instead of 0.05 to 0.1 gram) because of the low carboxylic acid content of the pitch fractions. Reproducibility was about four per cent.

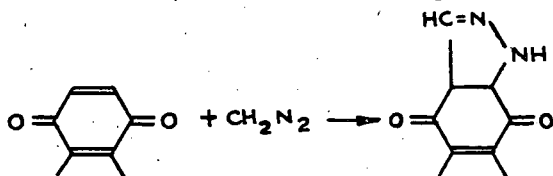
II. Non-aqueous titration. - A mixture of the sample (0.3 to 0.8 gram) with benzoic acid (0.015 to 0.025 gram) was titrated potentiometrically using the same solvent, titrant, and electrodes as in Method 1, I (above); the first major inflexion was taken as the end point. Reproducibility was about ten per cent.

#### 4. Ester Groups

The method employed by Knotnerus (7) for the determination of the saponification number of blown bitumens was adopted. Reproducibility was poor (about twenty per cent), probably because of the low solubility of the pitch fractions.

#### 5. Quinones

It is probable that much of the oxygen measured in the carbonyl determination is quinonoid. The increase in nitrogen content of samples following treatment with diazomethane could also be attributed to quinones - but only to 1,4-quinones of the types known to undergo addition with diazomethane to form pyrazoline rings (8, 9) - that is, "terminal ring" quinones:



A value for 1,4-quinones can therefore be calculated from the uptake of nitrogen.

#### C. Molecular Weights and Coking Values

Molecular weights were determined cryoscopically in phenanthrene, and coking values by the method of Charette and Girolami (10).

### RESULTS AND DISCUSSION

The solvent analysis of the pitch, the elementary analysis and coking values of the pitch and pitch fractions, and the molecular weights of the soluble fractions, are given in Table I. This shows that the percentage of oxygen tends to be higher in the less-soluble fractions of the pitch, and that decrease in solubility is accompanied by increase in molecular weight and coking value.

Table II summarizes the functional group analyses of the pitch fractions; values tabulated are the average of at least two determinations.

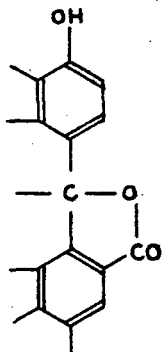
Close agreement for phenolic hydroxyl determined by non-aqueous titration and by mesylation was obtained for the crystalloids and the resinoids. The values for functional groups in the C<sub>1</sub> fraction are generally low (Table III), probably because of its insolubility. In this case the mesylation hydroxyl value is higher than the titration value and this may be due to the greater reactivity of the methane sulphonyl chloride or to the longer reaction time employed.

In comparison with the other techniques, methylation and acetylation gave lower values for phenolic hydroxyl.

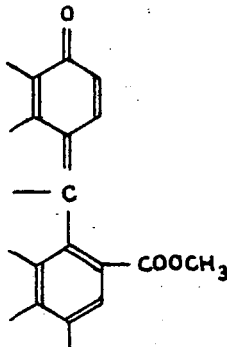
When methylated fractions were acetylated, higher overall hydroxyl values

were obtained than when either acetylation or methylation was used alone. On the other hand, when acetylated fractions were methylated, values were obtained similar to those with methylation alone, and infra-red examination of the methylated acetylated products revealed that all the acetyl groups had been eliminated. This elimination reaction was noted for pure compounds by Bredereck et al. (11). Results obtained by acetylation of methylated fractions suggest that methylation may make functional groups more accessible to acetic anhydride. Several types of hydroxyl groups appear to be present, probably of different acidities and/or steric disposition.

Carboxylic oxygen in the resinoids and  $C_2$  determined by hydrolysis of methylated fractions is higher than that measured by decarboxylation or non-aqueous titration, and is highest in the  $C_2$  fraction. High carboxyl and low hydroxyl (by methylation) values could be explained by lactones of the fluorescein type (12).



which, on treatment with diazomethane, give an ester



Such a reaction could account for the low phenolic (i.e. hydroxyl) values obtained with the  $C_2$  fraction.

Bearing in mind the relatively low accuracy of the decarboxylation and titration methods it is probable that the carboxylic acid contents of the resinoid and crystalloid fractions are negligible, and the methylation value for the resinoid fraction would again be due to the presence of lactones. The fact that there was little difference in the values given by these two methods for the carboxylic-acid content of the  $C_2$  fraction, indicates that these values are significant.

The resinoid and  $C_2$  fractions had the highest carbonyl contents. The three methods of measuring the extent of reaction with hydroxylamine gave similar results, indicating that nitrogen uptake was entirely in the form of hydrolysable oxime.

Calculation of 1,4-quinone oxygen from the nitrogen increase following methylation has given values lower than those for carbonyl oxygen (except with crystalloids), but of the same order. The results could be interpreted to mean

that much of the carbonyl is in the form of terminal-ring 1,4-quinones.

Diazomethane also forms pyrazolines with  $\alpha\beta$ -unsaturated ketones and aldehydes (8); but in the present investigation it is assumed that these are absent from high-temperature tar.

Ester groups appear to be absent from all fractions except the resinoid, which latter has an "ester-oxygen" content approximately equivalent to the content of carboxylic-acid oxygen measured by the hydrolysis of the methylated resinoids. This evidence supports the suggestion that methylation of a lactone had occurred.

Oxygen, as phenolic hydroxyl (by mesylation), carbonyl (by oxime formation), and carboxyl (by decarboxylation) is given as a percentage of the total oxygen (determined by the direct method) in Table III. It can be seen that for the resinoids the total functional-group oxygen is higher than, and for the crystalloids and  $C_1$  fraction lower than, the total oxygen; while for the  $C_2$  fraction the total functional-group oxygen is approximately the same as the total oxygen. The high value for functional-group oxygen in the resinoids could be explained, partly at least, by the possibility that mesylation will determine other groups in addition to phenolic ones. Non-aqueous titration - which gives the same value as mesylation - can determine certain terminal-ring, 1,4-quinones as "phenolic hydroxyl". The extent of such overlapping as this between the methods employed for functional-group analysis is difficult to estimate, and at present an approximate figure cannot be given for unreactive (i.e. ethereal) oxygen, although consideration of the results as a whole suggests that this should be low for the resinoids and the  $C_2$  fraction.

The  $C_2$  is the fusible fraction of highest molecular weight obtained by the solvent-extraction method used in this work, and it gives the highest yield of coke ( $C_1$ , being infusible, gives a char). Van Krevelen et al. (13) have shown that free carbon ( $C_1 + C_2$ ) of pitch is similar to a coking coal in its dilatometric properties, so that the  $C_2$  probably contains the more important coking constituents of pitch.

The present authors have separated the  $C_2$  into three parts by fractional precipitation of its pyridine solution with water (Table IV). As expected, the least soluble part had the highest molecular weight (832) and the most soluble the lowest (420). However, the coking values were similar for each part and the phenolic hydroxyl content was highest in the lowest molecular-weight fraction. Clearly, molecular size is not the only factor controlling either the insolubility of  $C_2$  in benzene or its high coking value. Results so far show that functional groups, of which phenolic hydroxyl is probably the most important, play a part.

#### CONCLUSIONS

- (1) The concentration of oxygen-containing functional groups is highest in the light-petroleum insoluble fractions and in particular in the  $C_2$ .
- (2) Phenolic hydroxyl, carbonyl, and carboxylic acid groups account for most of the oxygen in the pitch fractions examined.
- (3) Phenolic hydroxyl is the most important oxygen-containing functional group, whilst carbonyl oxygen and carboxylic-acid oxygen occur in approximately equal amounts except in the resinoid fraction, where the carbonyl oxygen is high (accounting for almost 50 per cent of the total) and the carboxylic-acid oxygen probably negligible.
- (4) The content of ethereal oxygen is probably low in the resinoids and the  $C_2$  fraction.
- (5) The "insolubility" and high coking value of the  $C_2$  fraction depend not only on

its high molecular weight but also on the presence of reactive centres, one of which is probably the phenolic hydroxyl group.

#### ACKNOWLEDGEMENTS

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TABLE I. ANALYSIS AND PROPERTIES OF PITCH AND PITCH FRACTIONS

Pitch Fraction	% Total Pitch	Elementary Analysis					Mol. Wt.	Coking Value, %
		C	H	O*	N	S		
Crystalloids	38.5	92.0	5.6	1.7	1.1	0.4	230	10.8
Resinoids	18.5	90.2	4.8	2.8	2.2	0.4	381	58.3
C <sub>2</sub>	15.5	86.7	4.2	4.3	2.6	0.6	608	85.5
C <sub>1</sub>	27.5	91.6	2.9	2.6	1.4	0.7	-	94.1
Pitch	100	91.4	4.5	2.4	1.3	0.5	-	56.6

\* Direct method.

TABLE II. FUNCTIONAL GROUP ANALYSES

Method of Analysis Fraction	Oxygen as Phenolic Hydroxyl, %						Oxygen as Carboxyl, %			Oxygen as 1,4-bonyl, %	Oxygen as 1,4-Quinone, %	Oxygen as Esters, %
	Non-aqueous titration	Methyl-ation	Acetyl-ation	Methyl-ation followed by acetyl-ation	Acetyl-ation followed by methyl-ation	Methyl-ation and hydrolysis	Decarboxylation	Non-aqueous titration	Oxime formation	Nitrogen content of methylated sample	Saponification	
Crystalloids	0.90	0.95	0.36	0.54	0.75	0.46	< 0.1	0.19	0.25	0.41	nil	
Resinoids	1.9	1.9	0.83	0.63	1.27	0.52	< 0.1	< 0.1	1.34	1.00	0.43	
C <sub>2</sub>	2.0	2.5	0.57	1.2	1.51	0.59	1.47	0.93	1.1	0.86	nil	
C <sub>1</sub>	0.55	1.2	0.57	0.49	0.95	0.64	0.26	0.60	0.44	0.39	nil	
Pitch	-	2.1	0.39	0.96	-	-	0.25	0.23	0.53	0.35	-	

TABLE III. FUNCTIONAL-GROUP OXYGEN AS PERCENTAGE  
OF TOTAL OXYGEN

Fraction Functional Groups	Crystalloids	Resinoids	C <sub>2</sub>	C <sub>1</sub>
Phenolic hydroxyl (mesylation)	56	68	58	46
Carbonyl (oxime formation)	15	48	22	17
Carboxylic acid (decarboxylation)	11	3	22	23
Total	82	119	102	86

TABLE IV. PRECIPITATION PRODUCTS FROM C<sub>2</sub> FRACTION

Fractions	Yield, as % of C <sub>2</sub> Fraction	Colour	Mol. Wt.	Oxygen, as Phenolic Hydroxyl, %	Coking Value, %
C <sub>2</sub> /1	46.6	Black	830	1.3	89.7
C <sub>2</sub> /2	26.6	Dark brown	545	2.2	89.1
C <sub>2</sub> /3	26.8	Reddish- brown	420	2.9	86.2